UDC 66

1D/0D HYBRID N-DOPED CARBON NANOTUBE/PARTICLE COMPOSITE AS A HIGHLY EFFICIENT ELECTROCATALYST TOWARDS OXYGEN REDUCTION REACTION

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Abstract

Optimization of microstructure is the key to design nitrogen-doped carbyl oxygen reduction electrocatalyst.One-dimensional /0D composite catalyst (L-Fe-CN-C) was prepared from graphite carbon nitride, ferric chloride and carbon black. The synthesized catalyst consists of nitrogen doped carbon nanotubes and nanoparticles. The catalyst showed good ORR activity and high selectivity through modulation. This work provides a reasonable strategy for the controllable synthesis of nitrogen doped carbon ORR catalysts with hierarchical structure and good performance.

1. Introduction

Since a single metal atom has a high surface free energy and cannot exist independently, it is generally confined to the base material by the strategies of space limiting, atomic anchoring, defect trapping, etc., so the base material is essential in the synthesis and electrochemical reaction of the single atomic material. More importantly, the structure and composition of base materials also significantly affect the electrochemical behavior of sulfur cathode. Fuel cells and metal-air batteries have been projected as the promising substitutes to the combustion engine on transportation devices for several decades, ascribing to the high energy density, steady working voltage, high efficiency and safety, abundant resources of hydrogen and transition metals, and the environmental benignity[1-3]. metal-nitrogen codoped carbon materials (M-N-C) [4,5] are two kinds of typical ORR catalysts to be developed as the potential alternatives to the Pt-based catalysts due to their promising electrocatalytic performance and low cost. The distribution of electron on the graphene is regulated due to the different electronegativity of nitrogen and carbon atoms. Hence, these configurations, especially pyridinic N, graphitic N and M-Nx structures are widely recognized as the ORR active sites of the M-N-C catalysts[6-8]. interestingly, Yang et al. designed an iron-tetrapyridophena-zine molecular complex and illustrated it to be an Fe precursor for the synthesis of Fe-SACs. A notable exception is the work of Chen, Li, and co-workers, who synthesized isolated Fe-SA supported on ordered mesoporous N-doped carbon (Fe1/N−C) for the reduction of nitro compounds. [9-12]The M-N-C catalysts are typically prepared by pyrolyzing precursors consisted of transition metal, nitrogen and carbon elements from salt and nitrogen-contained organic compounds. The organic compounds are decomposed at a high temperature and then deposited as graphene-like layers to form carbon nanotubes, sheets or particles with the facilitation of metal species.

In addition, the research group has also done some exploratory work in the early stage, such as using scanning electron microscopy (SEM) to characterize the morphology and size of MET-1000 catalyst. As shown in Figure 1a, the MET-1000 catalyst exhibits a graphene-like lamellar structure. As shown in SEM FIG. 1b at high resolution, MET-1000 catalyst also has abundant pore distribution, indicating that the prepared MET-1000 catalyst has a three-dimensional porous nanonetwork structure.

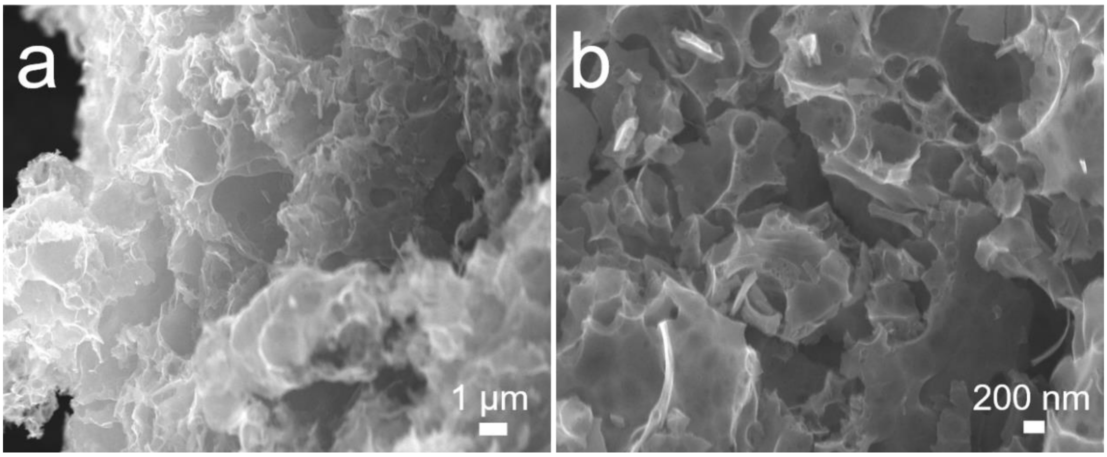

Fig. 1 SEM diagram of MET-1000 catalyst

The MET series catalyst was electrochemical tested in 0.1 M KOH under saturated oxygen condition. The ORR performance was measured by cyclic voltammetry, as shown in Figure 2. The MET-1000 catalyst had a half-wave potential of 0.84 V vs. RHE (E1/2) and a limiting current density (JL) of 5.6 mA cm-2. Over MET-900 catalyst (E1/2= 0.88v vs. RHE, JL= 5.1mA cm-2) and MET-1100 catalyst (E1/2= 0.88v vs. RHE, JL= 4.9mA cm-2), It is similar to the performance of Pt/C catalyst (E1/2= 0.85V vs. RHE, JL=5.5 mA cm-2), indicating that MET-1000 catalyst has excellent ORR performance.

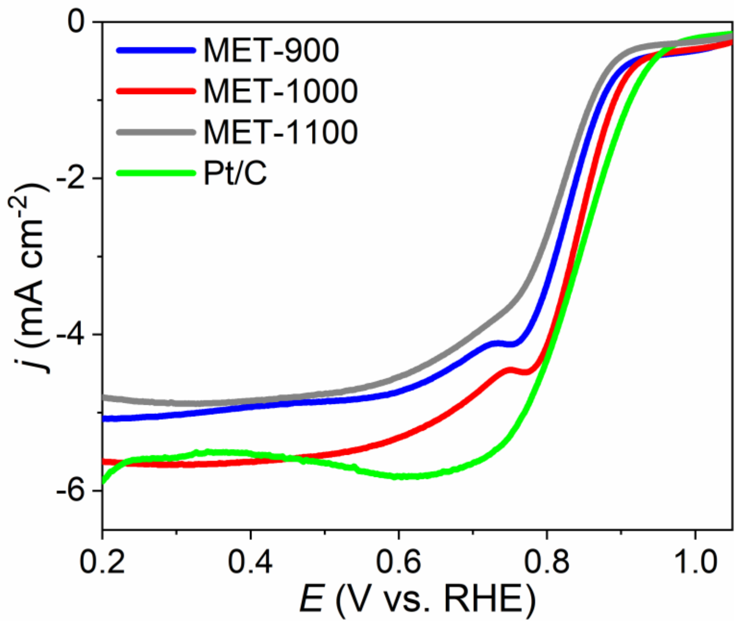

Fig. 2 LSV curves of MET series catalysts and Pt/C catalysts

2. Experimental

First of all, the graphite carbon nitride g-C3N4 is made of pyrolyzing melamine at 550℃ in Muffle furnace for 4 h. Then 6 g of g-C3N4 and 3 g of FeCl3•6H2O are dispersed in ethanol and stirred for 24 h at 50°C, ensuring that iron ions chelate g-C3N4 table. The precursor is made of evaporated ethanol. Precursor of 3 g and 0.8 g of carbon black is thoroughly and catalyst by pyrolyzing fabricated the mixture in a nitrogen atmosphere at 600 ° C 2 h and 850 ° C for 3 h. Target Fe-CN-C immersed in 0.5 obtained catalyst sulfuric acid solution at 80°C for 10 h leach unstable species.

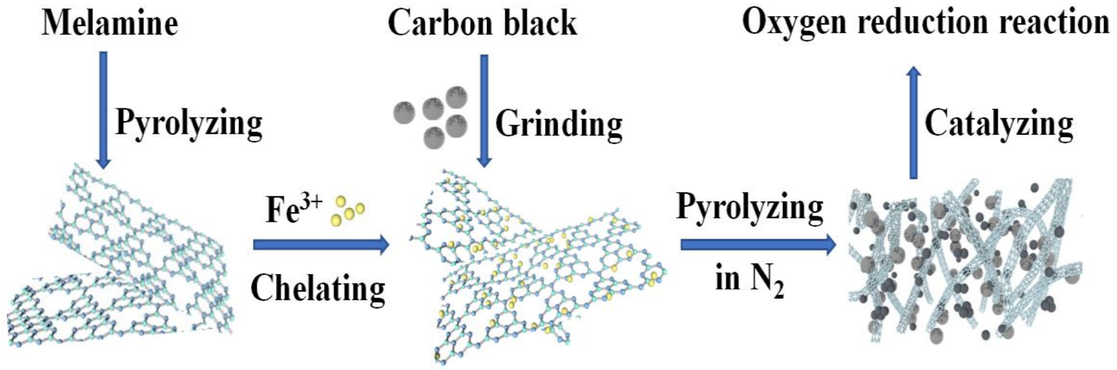

Fig. 3 Schematic illustration for the fabrication of the L-Fe-CN-C catalyst

3. Results and discussion

The morphology of catalysts was observed by SEM and TEM. As shown in Fig. 4a, Fe-CN is consisted of pure carbon nanotubes with large diameters ranging from 100 nm to 300 nm. However, the morphology of Fe-CN-C was dramatically changed with the addition of carbon black into the precursor. As presented in Fig. 4b, the

Fe-CN-C is consisted of three kinds of carbon materials. One is carbon nanotubes with ~25 nm of diameter which is very smaller than those in Fe-CN, showing that the growth of nanotubes was suppressed by the added carbon black. There exist other two kinds of nanoparticles in Fe-CN-C beside the nanotubes. The advantage of this microstructure is that more surficial active sites can be exposed due to the greater specific surface area from the smaller particles. Moreover, the space in the material can be effectively utilized because that the tunnels constructed by the nanotubes are well filled by the carbon nanoparticles. It should be the metallic Fe or Fe3C in the core as the growth center for the carbon nanoparticles which are further protected by the graphite layers from dissolution and can be detected by XRD after acid treatment.

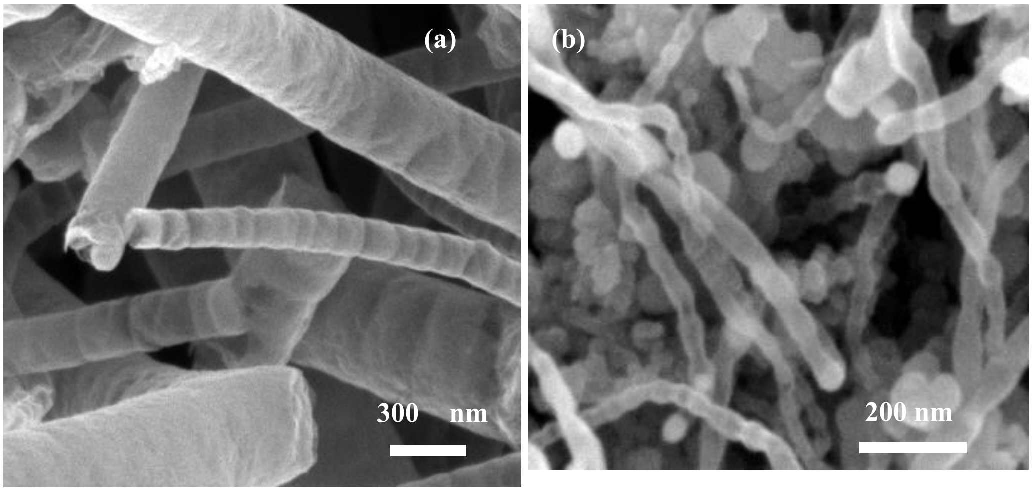

Fig. 4 SEM image of (a) Fe-CN, (b) Fe-CN-C

The ORR activity of the catalyst was determined by linear sweep voltammetry (LSV) in 0.1 M KOH oxygenated solution. As shown in Figure 5, Fe-CN has an ORR half-wave potential of 0.810 V (E1/2) and a finite diffusion current density of 3.523 mA cm-2. The addition of carbon black increased the catalytic activity of Fe-CN-C, with E1/2 of 0.845 V and jd of 5.301 mA cm-2. It can be thought of as the result of two positive factors. First, Fe-CN-C consists of smaller nanotubes and nanoparticles with a higher specific surface area than Fe-CN. Secondly, XPS analysis showed that the content of pyridine N with ORR activity in Fe-CN was higher than that in Fe-CN. The half-wave potential of L-Fe-CN-C was further translated to 0.850 V, comparable to 0.853 V for the reference Pt/C catalyst. The ultimate diffusion current density of L-Fe-CN-C increased to 6.224 mA cm-2, higher than 5.112 mA cm-2 for Pt/C. The main N configurations in L-Fe-CN-C are ORR reactive pyridine and graphite C-N structure. The mesoporous stratification of L-Fe-CN-C also contributes positively to the catalytic performance, as the mesoporous tunnel facilitates mass transfer and accessibility of the active site.

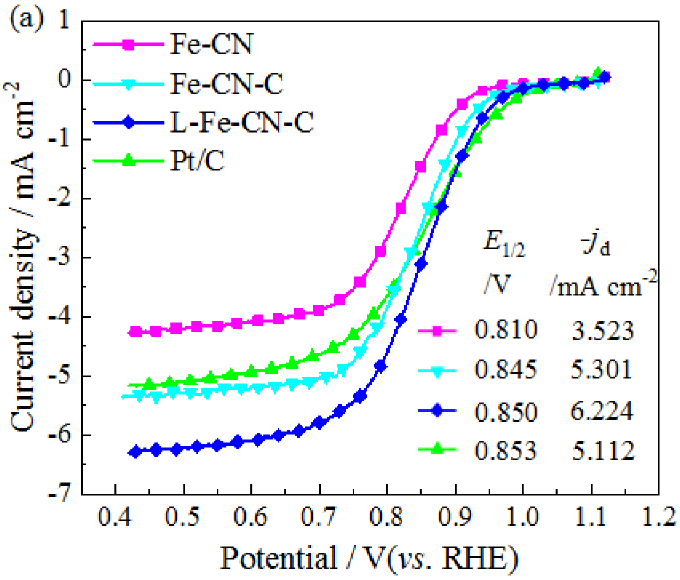

Fig. 5 LSV curve of various catalysts to ORR

4. Conclusions

In conclusion, the two-dimensional structure of carbon materials is mainly layered and mesoporous. This work provides a feasible way to prepare nitrogen-doped carbon-based ORR catalysts with higher electrocatalytic activity and broadens the selection range of expensive alternatives to Pt-based catalysts in the field of renewable energy.

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